NEW APPROACH TO IDENTIFY COMPATIBILITY OF MATERIALS FOR CONCRETE RELATED TO EARLY STIFFENING

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Abstract

The measurement of the evolution of mechanical characteristics during the setting period of concrete is needed to control the schedule of construction (pumping, placement, finishing and saw-cutting). This evolution is affected by the compatibility (or incompatibility) of the materials used, such as chemical admixtures and cementitious materials. The Vicat test is the standard test for setting. The information obtained by this test (initial and final set) is largely insufficient, for example, to determine the time during which the material can be pumped or extruded. Our study monitored the cement paste setting period through the variation of an intrinsic material parameter, yield stress. The rheological measurements used were stress growth and the mini-slump. A large set of cements, three supplementary cementitious materials, and two Type A water reducers were used as part of a larger project sponsored by Federal Highway Administration (FHWA) aimed at developing a methodology to select materials for pavement applications. This study's goal was to determine the feasibility of using either stress growth with a rheometer or mini-slump test to determine incompatibility between materials. The setting times of the cement pastes were monitored for early stiffening (less than 60 minutes) as well as delayed stiffening (several hours). The results of these experiments are discussed and compared. We show that the proposed tests are more sensitive to the setting evolution of cement paste than the Vicat test and provide useful early age information.

1. INTRODUCTION

Today, concrete is composed of more than just water, cement and aggregates. Most concretes include chemical admixtures and supplementary cementitious materials (SCM). This increased complexity leads to difficulties in predicting the fresh and hardened properties of a concrete. The complexity is enhanced by the chemical or physical incompatibility of the various components. These incompatibilities can be revealed by early stiffening, poor consolidation, early-age cracking, and lack of proper air entrainment. Federal Highway Administration (FHWA) sponsored [1] a comprehensive study to develop a methodology to

pre-screen materials to avoid problems on the field. The study concentrated in three properties: early stiffening or retardation, cracking, and air void system. This paper will only analyze the results obtained for early stiffening or retardation.

The methodology that was developed and that will be presented here deals with fresh cement paste and the evolution of properties, such as setting time, rheological behavior, heat evolution, and bleeding. The tests were conducted on cement paste. Comparison with mortar properties such as compressive strength or stiffening, as well as examination of the pore solution chemistry to attempt to correlate incompatibility with composition of the cement and chemical admixtures were performed and can be found in [1] but will not be discussed here.

2. MATERIALS USED

The approach selected was to use a wide variety of materials and several techniques to sort the cements into "bad" or early stiffening cements, "good" cements and in-between cements by using various techniques. The scope was then to attempt to find a correlation among the laboratory behavior of the cement, its field performance and its chemical composition. Six cements, two types of fly ash, a slag and two types of chemical admixtures or water reducer admixtures (WRA) were used. The cements were selected to straddle three characteristics: C_3A content, alkali content and gypsum/hemihydrate ratio. Table 1 shows the various levels.

Table 1: Commercial portland cement characteristics

Cement #	C_3A Content, %	Alkali Content, %	Gypsum-to-Hemihydrate Ratio	Contains Natural Anhydrite
1	6	0.56	1.50	Yes
2	12	1.06	0.08	-
3	10	0.38	0.07	-
4	11	0.53	1.05	-
5	10	0.92	4.11	-
6	6	0.56	0.58	Yes

The two fly ashes were: 1) Class C selected with a relative high C_3A (11.4 %) because it is most usually associated with setting and stiffening problems; 2) Class F selected with low loss on ignition (LOI) of 4 % by mass. A commercially available slag, grade 100 (ASTM C 989) was also selected. The two WRA were: WRA A lignin-based and WRA B sugar base. Both are type A (ASTM C 494) admixtures.

All the materials were characterized using x-ray diffraction, x-ray fluorescence, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The Blaine fineness and particle size distribution were also measured. The details of this characterization are available [1]. The cements were blended with fly ash (20 % replacement of cement by mass fraction) or slag (40 % replacement of cement by mass fraction).

All cement pastes were prepared with a water/cementitious ration (w/cm) of 0.5 unless otherwise indicated. The WRA A dosages were either 325 mL/kg (5 oz/cwt) or 650 mL/kg (10 oz/cwt) and the dosage of WRA B was 163 mL/kg (2.5 oz/cwt).

3.   METHODOLOGY USED

3.1   Tests used

Various measurements were done to characterize early stiffening or retardation. The test methods used are shown in Table 2.

Table 2: Tests conducted on cement paste

Information needed	Test Method
Yield stress and plastic viscosity	Minislump: two methods Rotational rheometer
Heat generation behavior	Isothermal conduction calorimetry
Setting behavior	Penetration of 2 mm diameter Vicat needle (AASHTO T 131)
Bleeding	Mass and volume of water decanted after initial set from a known volume and mass of cement paste
Mortar cube strength	ASTM C 109
Mortar air content	ASTM C 185
Mortar stiffening	ASTM C 359
Pore solution chemistry	Periodically up to 24 h. Analyses were conducted for sulfate, calcium, alkali and hydroxyl ion concentrations, and pH

In this paper we will concentrate on the tests related to workability or rheological behavior such as yield stress, heat generation, and the Vicat needle. The results of the other tests including uncertainties can be found in ref [1].

These tests were used to screen the "bad" combinations. Comparisons with the results obtained using mortar or concrete were used to validate the methodology to pre-screen the materials using cement paste and laboratory tests.

The yield stress was measured using a methodology developed at NIST using a parallel plate rheometer. This rheometer is composed of two serrated plates 0.4 mm apart during measurements. The bottom plate is fixed and the top plate rotated (imparting a shear rate on the material) according to two patterns controlled by a computer. The torque (related to shear stress) generated by the material located between the two plates is recorded. The temperature of the plates is controlled and was set at one of the following temperatures 21 °C, 32 °C or 10 °C. The most common method to measure rheological properties is by using the Bingham model defined by equation (1)

$$\tau = \tau_0 + \mu\dot{\gamma} \tag{1}$$

where τ is the shear stress applied to the material (in Pa), τ_0 is the yield stress (in Pa), μ is the plastic viscosity (in Pa·s), and $\dot{\gamma}$ is the shear strain rate (also called the strain gradient) (in s^{-1}).

It was shown in previous work [2, 3] that the monitoring of the rheological property evolution using this model leads to aberrations such as negative plastic viscosity, i.e., a negative slope when shear stress is plotted versus shear rate. Therefore, another method was selected, stress growth measurement. The *stress growth test* is characterized by the material being sheared at a very low shear rate (0.01 s^{-1} here). This shear rate was selected as the

minimum shear rate possible with the available rheometer. The stress is recorded versus time for 3 min to 5 min. The end of the linear behavior defines the real yield stress (Figure 1) but it is not possible to measure this point with the rheometer available due to the few points recorded before the peak value especially at very early age (time < 2 h). The peak phase, defined by the peak value, is easily measured and so is used as a good approximation of the yield stress [4]. Only a small error is introduced by selecting the peak itself instead of the end of the elastic period as a measure of the yield stress. It should be stated that the lower the shear rate the more accurate is the measurement of the yield stress as more points are obtained before the peak is reached. A value for the shear rate lower than the one used in this study would be desirable. The yield stress evolution is monitored by plotting the peak value (B point of Figure 1) of the shear stress at various times (Figure 2) after water and cement are in contact. The time, t_s in Figure 2, indicates a sharp increase in the yield stress versus time. This value is taken as the initial setting time by this method.
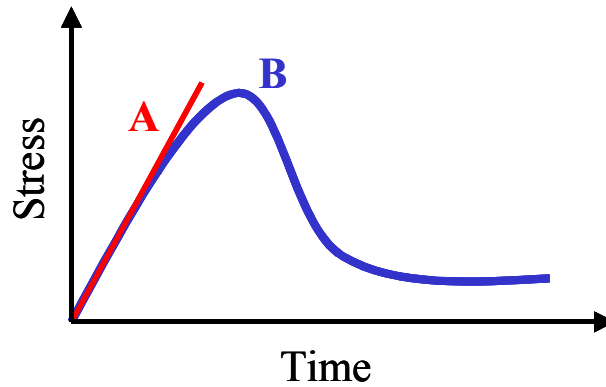

Figure 1: Stress growth measurement: Point A is the end of the linear portion, i.e., elastic portion, and is the true yield stress point; Point B is the peak point and it is taken as an approximation of the yield stress because it is more reliably identifiable parameter.
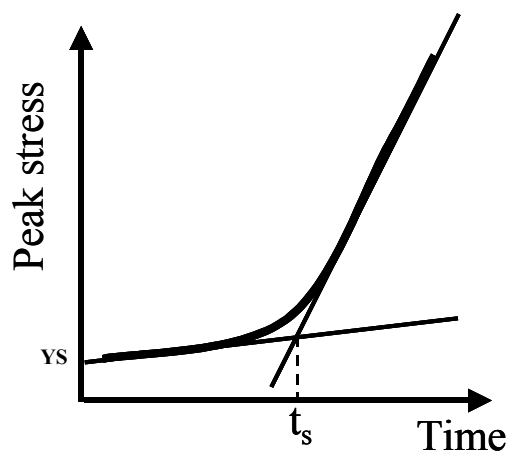

Figure 2: Typical curve for the peak stress from Figure 1 versus time obtained for stress growth experiments. The time, t_s, is considered to be the initial setting time. YS is the initial yield stress.

The mini-slump [6, 7] is a cone with the following dimensions: bottom diameter of 38 mm, a top diameter of 19 mm, and a height of 57 mm. The mini-slump cone is filled with the cement paste, then the cone is lifted and the area of the patty formed is calculated from the measurements of four diameters. A larger patty area indicates a high workability or a low yield stress. To monitor the workability loss, the area or an average diameter could be plotted versus time. The minimum area that can be measured is an area equal to the bottom area of the mini-slump, i.e., the cement paste did not flow at all under its own weight.

The heat generation was measured by isothermal calorimetry at 21 °C. Dry ingredients and fluids were introduced separately into the calorimeter until their temperatures had stabilized. The fluids were then introduced into the powders, without mixing, and data collection was started. Output from the instrument is power (J/g·h) as a function of time. A typical set of plots is shown in Figure 3. Initial set is indicated as the time when power starts to increase at the beginning of the second peak.
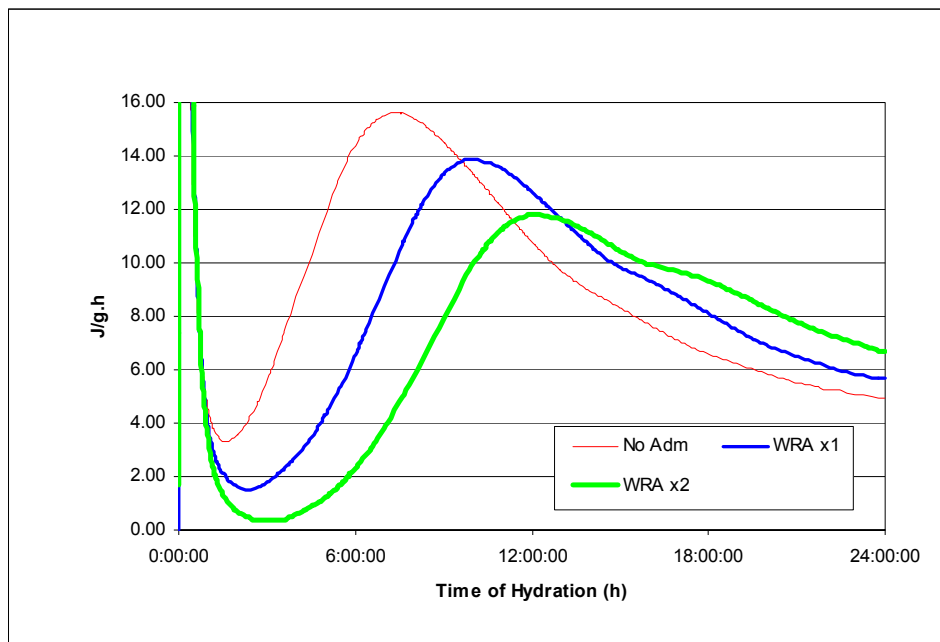

Figure 3: Typical calorimetry plots showing the effects of increasing admixture dosage.

The Vicat device used is described in ASTM C191-99[3]. The needle is on a 300 g moveable rod and has a diameter of 1 mm ± 0.05 mm. A specimen of fresh cement paste is prepared and placed in a frustum 40 mm in height. Initial setting time is considered in this paper as the time when the needle penetration is 39 mm ± 0.5 mm. The final setting time corresponds to less than 0.5 mm penetration. This is not exactly as described in the standard test, where the needle penetration at initial setting time is 30 mm ± 0.5 mm.

4.   RESULTS AND DISCUSSION

The scope of this study was to develop methodologies to pre-select materials suitable for pavement concrete. The issue was the detection of potential incompatibilities between cement, chemical admixtures and supplementary cementitious materials. These incompatibilities usually result in early stiffening or severe retardation. All the tests described above could detect some aspect of the early stiffening or retardation, but are they capable of detecting the influence of chemical admixtures or temperature? Or should the following question be asked: What is the mechanism causing incompatibility? The obvious answer could be some chemical reactions that lead to either early stiffening or retardation. Unfortunately, the chemical reactions that contribute to the problem are too complex and inter-related to be correctly interpreted and generalized for performance prediction. Also, if the results of this study are to be used beyond the selected materials, other chemical admixture compositions may need to be considered. This would be a daunting task impaired by the proprietary composition of most chemical admixtures. Therefore, there is a need for properly selected tests that will flag problems before full production is launched.

The data were examined by comparing the various tests to determine the best methodology to determine the materials combinations that could create problems such as early stiffening or retardation. Figure 4 shows the comparison between initial and final setting time using the Vicat method. It is clear from the high correlation coefficient that the two values are correlated. The slope of the fit is 1.06 and there is an offset of 1.74 h. This implies that the only significant difference is that the final setting time is 1.74 h after the initial setting time. It could be inferred that only the initial setting time needs to be measured to rank the cement paste behavior.

Figure 5 shows the comparison between the stress growth set time (t_s from Figure 2) and the initial setting time as measured by Vicat. The linear correlation has a correlation factor of 0.72. It should also be taken into consideration that there is about an error of 30 min for either the stress growth or the Vicat needle setting time. The setting time measured with stress growth is about 33 % lower than measured using the Vicat needle. These results are not too surprising as the two methods measure "setting time" by monitoring different phenomena. The Vicat needle applies a constant stress of 2.9 MPa ($300 \cdot 10^3$ kgf/m^2) determined by the mass and area of the needle. The initial setting time is determined when the cement paste can sustain a stress higher than this constant stress. Therefore, it could be stated that the yield stress of the cement paste needs to be higher than 2.9 MPa to be observed using a Vicat needle. On the other hand, the stress growth measurement can measure smaller stresses (as low as 10 Pa) monitoring their evolution before and after setting time. Therefore, the yield stress observed could be significantly smaller than with the Vicat needle and could be observed earlier. This could be explained by the fact that the Vicat test definition of setting is when the paste can sustain a stress higher than 2.9 MPa, with no monitoring of the stress evolution before that value is reached. On the other hand, the stress growth method is not bound by such a high preset value to select the yield stress.
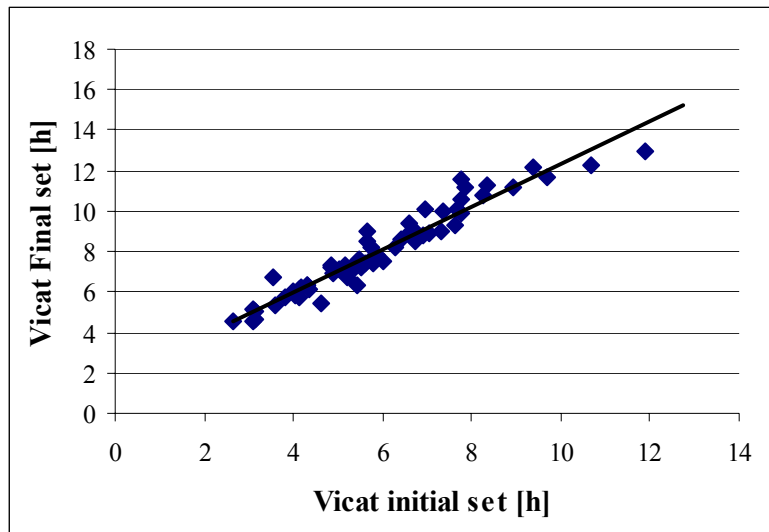
Figure 4: Correlation between Vicat set times. The value of the coefficient R^2 of the fitted line is 0.93. The error on the data is estimated by repeat testing to ± 0.5 h.
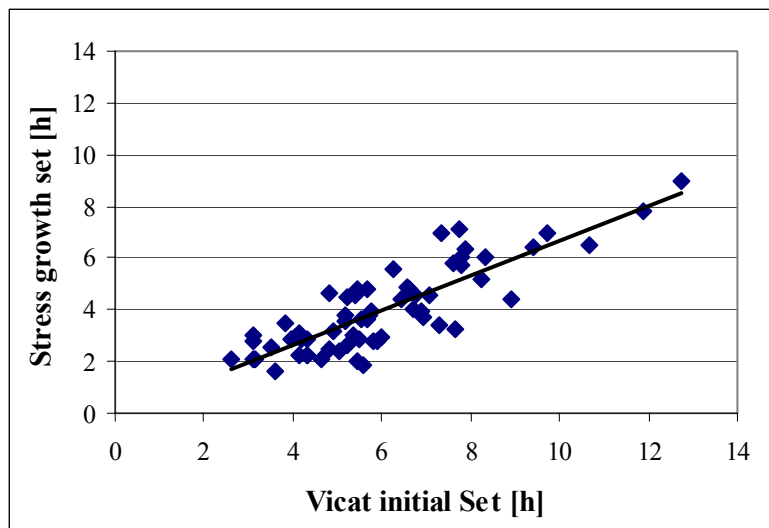

Figure 5: Comparison between the stress growth initial set time (sharp increase of the yield stress) with the Vicat Initial set time. The value of the coefficient R^2 is 0.72 for a linear fit. Error of either value is estimated at ± 0.5 h

Figure 6 shows the relationship between the initial yield stress measured using stress growth and the initial mini-slump. The complete assessment of the uncertainty was not conducted but from previous work the error on the minislump is estimated to $\pm 10 \cdot 10^2$ mm^2 and the yield stress by stress growth would be 50 Pa [3]. The first mini-slump was measured 15 min after water and cement were in contact. The initial mini-slump could be related to the initial flow behavior that includes a combination of the rheological properties of the cement paste. From Figure 6, it seems that there is a relationship but it is clearly linear. At low mini-slump values, there is wide range of yield stresses measured with the stress growth test, while

there is a wide range of mini-slump values for narrow range of yield stresses for mini-slumps larger than $50 \cdot 10^2$ mm^2. It should be noted that the mini-slump will not record any changes in the surface area until the yield stress is lower than the weight of the cement paste in the cone. For our material, the weight is 302 Pa. At this point, the cement paste will not flow when the mini-slump is lifted and the area recorded will be similar to the area of the bottom cone, i.e., $23 \cdot 10^2$ mm^2. The stress growth can measure higher yield stresses and therefore is able to distinguish between cement pastes with the same mini-slump value close to $23 \cdot 10^2$ mm^2. In Figure 6, it can be observed that there is still a large scatter for mini-slump areas below $50 \cdot 10^2$ mm^2, i.e., the same mini-slump is related to widely different yield stresses as measured with the stress growth method. One hypothesis that could be advanced is that the friction of the cement paste on the mini-slump plate interferes with the flow of the paste for yield stresses above 100 Pa, preventing the cement paste from creating a larger patty. This hypothesis should be verified by testing a cement paste with the same yield stress using various surfaces, or by reducing significantly the friction between the cement paste and the surface. This later could be achieved by using a very smooth surface.
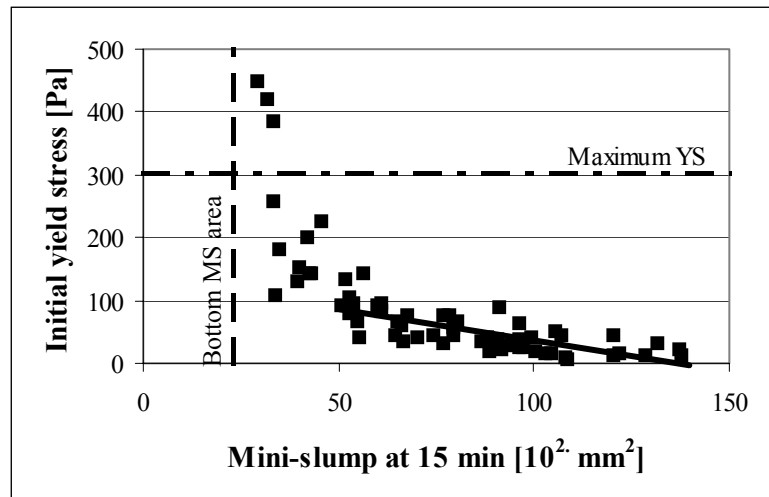

Figure 6: Comparison between the initial yield stress measured by stress growth and the Vicat Initial set time. The "Maximum YS" refers to the maximum value measurable with the mini-slump (see text). The "Bottom MS area" is the area of the mini-slump cone. The fit line is valid only for mini-slump higher than $50 \cdot 10^2$ mm^2.

Figure 7 shows the comparison between the initial setting time as defined by calorimetry and the initial setting time defined by the Vicat tests and the stress growth measurements. The correlation is not very good and there is some scatter even if the uncertainty of about 0.5 h is taken into account. Also the calorimeter time is higher than the Vicat time and significantly higher than the stress growth. As discussed previously the stress growth time is lower than the Vicat time.
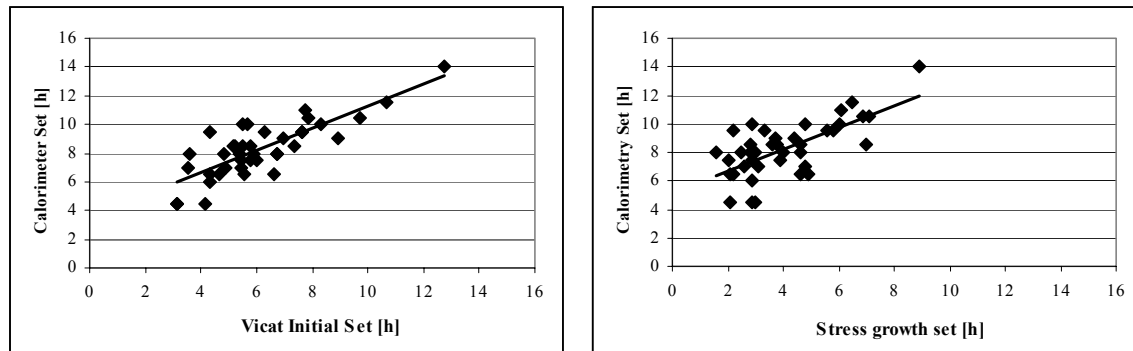
Figure 7: Comparison between the initial setting time as measured by the Calorimetry and by the Vicat. The value of the coefficient R^2 is 0.66 for a linear fit with the Vicat tests and 0.46 for the stress growth.

From the discussion above, we can see that there are some correlations between the various tests, but it is not obvious what value should be selected for each tests that will separate all the cements into categories, such as early stiffening, retardation or normal. The operator would have to determine what are the limits. Another approach is by ranking: which cement sets first and which last. The ranking obtained by the various methods are similar as shown in Table 3. In this table, only the results for the cements with no additives are shown as an example. In ref [1], all the data can be found. In Table 3, Cement 1P and 6P are only found in the 1st three positions while cements 3P and 4P are only found in the last three positions. This could be interpreted that cement 1 and 6 are retarded or slow setting while cement 3 and 4 are fast setting and potentially could show problems of early stiffening. The case of cement 2 is interesting as it has a slow setting time with Vicat but a high setting time as measured by stress growth and the mini-slump. Cement 4 and 5 are in the middle ranking between 3rd and 5th on most tests.

The addition of SCM was examined with cements 1 and 6. Table 4 shows the ranking obtained with the various tests. Although the ranking is not the same, trends are clearly seen. For cement 6, all the addition of slag results in a slower setting time compared to the plain cement (P). For cement 1, the ranking of the various additives using any of the methods is almost identical. The only difference is that the mini-slump reversed 1S and 1F. Therefore, as a first approximation it seems that any of these methods could be used to rank materials performance.

Table 3: Ranking of the neat cements (P= plain or neat), i.e., no addition of WRA or SCM. Calorimetry tests were not conducted on plain cements.

Type of Measurement	Cement						Order selected
Stress Growth, t_s	1P	6P	5P	3P	4P	2P	Low --> high
Vicat Init	2P	1P	6P	5P	3P	4P	Slow--> fast
Vicat Final	2P	1P	6P	4P	3P	5P	Slow--> fast
Mini-slump	1P	6P	3P	5P	4P	2P	Slow--> fast

Table 4: Classification of cement 6 and 1 with addition of SCM. S= slag ; F = Class F Fly Ash ; C= Class C Fly Ash ; P= Plain or neat cement. The performances are classified from slower (top) to faster (bottom).

Type of Measurement	Stress Growth	Vicat Initial	Mini-slump	Calorimetry
Cement type	6F	6C	6S	6C
	6S	6S	6F	6F
	6P	6F	6C	6S
	6C	6P	6P	6P
	1C	1C	1C	1C
	1S	1S	1F	1S
	1F	1F	1S	1F
	1P	1P	1P	1P

CONCLUSIONS

The screening of materials for pavement concrete is paramount to avoid problems in the field. The complete characterization of the materials, cement, chemical admixtures (WRA) and supplementary cementitious materials (SCM), should provide the information needed to determine whether or not a combination of materials will result in early stiffening or retardation. Unfortunately, at this point only rough estimates are possible due to the proprietary nature of the WRA and the variability of the cements and the SCMs. This study investigated the feasibility of using laboratory tests on cement paste to flag potential problems in setting time. The tests selected and discussed here are related to rheological properties, such as yield stress evolution. The tests were: stress growth with a rheometer, mini-slump, Vicat needle, and calorimetry.

It was shown that the results from these tests are correlated and that they rank the cement paste mixtures (with and without SCM) in approximately the same order. A protocol could be established using these tests to screen the materials.

ACKNOWLEDGEMENTS

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